

Spectroscopic study of spin-dependent exciton formation rates in π -conjugated semiconductors: Comparison with electroluminescence techniques

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It has been found in recent measurements that the singlet-to-triplet exciton ratio in organic light-emitting diodes (OLEDs) is larger than expected from spin degeneracy, and that singlet excitons form at a larger rate than triplets. We employed the technique of optically detected magnetic resonance to measure the spin-dependent exciton formation rates in films of a polymer and corresponding monomer, and explore the relation between the formation rates and the actual singlet-to-triplet ratio measured previously in OLEDs. We found that the spin-dependent exciton formation rates can indeed quantitatively explain the observed exciton yields, and that singlet formation rates and yields are significantly enhanced only in polymer OLEDs, but not in OLEDs made from the corresponding monomer.

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I. INTRODUCTION

The maximum possible internal quantum efficiency, η_{\max} , of fluorescent-based organic light-emitting diodes (OLEDs) occurs when the probability that the injected carriers form excitons and the quantum yield for singlet emission are both unity. η_{\max} is then determined by (and identical to) the fraction, f_s , of injected electrons and holes (or negative and positive polarons, respectively) that pair to form emissive spin-singlet excitons, rather than nonemissive triplet excitons. If the process by which these excitons form were spin independent, then η_{\max} would be limited to 25% based on spin degeneracy. However, recent reports indicate that η_{\max} in OLEDs ranges between 22% to 83%.^{1–8} The exact value of η_{\max} and the reason for this variation, however, have remained controversial. Indeed, even the notion that η_{\max} can be larger than 25% is currently not universally accepted.⁸

The following two entirely different experimental approaches have been employed to study spin-dependent exciton formation for OLEDs and thin films:

(i) Experiments^{1–3,5,7,8} that determine the *singlet generation fraction* f_s directly in live OLEDs. For fluorescent devices, typically only the singlet emission can be measured, information on triplet density is missing, and rather involved models have to be employed to obtain f_s .³ Wilson *et al.*, however, have recently shown⁵ that in OLEDs made from organic semiconductors that exhibit spin-orbit coupling, the strong intersystem crossing implies that both singlet and triplet emission (fluorescence and phosphorescence) can be simultaneously observed. This could be used to reliably determine f_s by comparing the relative intensities of fluorescence to phosphorescence for optical excitation (where initially only singlet excitons are formed) with that for electrical excitation (where both singlet and triplet excitons are formed). Importantly, they found $f_s=57\%$ for devices made from a platinum-containing polymer, but $f_s=22\%$ for the corre-

sponding monomer OLEDs. This suggests that exciton formation is spin independent for the monomer, but that a spin-dependent formation process is effective in the polymer.

(ii) Experiments^{4,6,9} that measure the ratio, $r=k_S/k_T$ of the spin-dependent *exciton formation rates* for singlet and triplet excitons, respectively. Such experiments manipulate the spin state (using electron-spin-resonance techniques) of the pairing polarons, and measure the effect on exciton formation rates. These experiments consider photogenerated polarons in the film and use the fact that antiparallel spin polaron pairs can either form singlet or triplet excitons, whereas parallel spin pairs can only form triplets. These optically detected magnetic-resonance (ODMR) techniques are modulation experiments where the resonant μ -wave field is periodically turned on and off. Since the experiment is performed at low temperature, spin alignment is conserved during the half wave with μ -wave field off, and polaron recombination/exciton formation obeys spin statistics. However, during the half wave with μ -wave field on, spin-1/2 resonance leads to rapid spin flips of the recombining polarons. Spin alignment is therefore not conserved, and each pair may choose whether to form singlet or triplet exciton. It can easily be shown^{4,6} that this leads to enhanced formation of the exciton with a larger formation rate (leading to a positive ODMR signal), at the expense of the more slowly forming exciton (that gives a negative ODMR). In addition, the overall polaron recombination rate is enhanced, since the fast channel becomes allowed for all polaron pairs. Therefore, changes occur in the photoinduced absorption (PA) from the triplet state, as well as the fluorescence from the singlet state upon magnetic resonance. In particular, from the μ -wave-induced change in PA of the polaron pairs, $r=k_S/k_T$ could be determined.⁴

Using ODMR, it was found that r is a monotonously increasing function of the conjugation length (CL), and, by extrapolation, that $r \approx 1$ for small molecules and monomers.⁶

Electroluminescence and magnetic-resonance experiments therefore lead to the same qualitative conclusions, namely that exciton formation is spin independent for the monomer, but that a spin-dependent process is effective in the polymer. However, it has not yet been shown that the r values measured by ODMR can be used for quantitative predictions of η_{\max} in OLEDs. It is especially important to study the quantitative relation between r and η_{\max} , since the experimental conditions of the two experiments are quite different, e.g., ODMR experiments have only been performed at low temperature and zero electric field. In addition, ODMR experiments are typically performed on thin-film samples rather than live OLEDs.

We have previously shown⁴ that *if spin randomization occurs during exciton formation*, a simple rate equation treatment leads to the following relation between r and η_{\max} :

$$\eta_{\max} = \frac{r}{r+3}, \quad (1)$$

otherwise $\eta_{\max}=25\%$, independent of the value of r . Examples of spin-randomizing processes include spin-orbit coupling, spin-lattice interaction, or competition between exciton formation and dissociation.

It therefore appears to be a simple matter to compare ODMR predictions of η_{\max} through Eq. (1) to those measured by Wilson *et al.* However, it is not possible to perform both experiments on the same compounds: The method by Wilson *et al.* relies on spin-orbit coupling for the observation of both fluorescence and phosphorescence, whereas spin randomization due to spin-orbit interaction is detrimental to the ODMR experiments. We have therefore chosen to perform our ODMR measurements on compounds very similar to those used by Wilson *et al.* except for the Pt-containing group. Here we show that the r values measured by ODMR can indeed quantitatively explain f_S measured using the method of Wilson *et al.* on live OLEDs. We thus conjecture that the spin-dependent exciton formation rates are the cause of $\eta_{\max} > 25\%$ observed in OLEDs.

II. EXPERIMENTAL

We measured three π -conjugated semiconductors, namely (i) the Pt-containing polymer shown in Fig. 1(a), (ii) a very similar polymer without the Pt-containing group referred to as “organic polymer” [Fig. 1(b)], as well as (iii) its corresponding monomer [Fig. 1(c)]. The 5,8-diethynyl-2,3-diphenylquinoxaline unit and its Pt-containing polymer were prepared according to published procedures.^{10,11} The organic polymer was synthesized by palladiumcatalyzed polycondensation of 1,4-bis(*n*-octyloxy)-2,5-diiodobenzene and 5,8-diethynyl-2,3-diphenylquinoxaline in a 1:1 ratio, whereas the model monomer was prepared by cross-coupling reaction of 4-iodoanisole with 5,8-diethynyl-2,3-diphenylquinoxaline in a 2:1 ratio.

For measuring r , we employed the PA and PA-detected magnetic-resonance (PADMR) spectroscopies. The PA technique has been widely used in π -conjugated materials for studying long-lived photoexcitations such as polarons and triplet excitons.¹² Two light beams are used in PA; one to

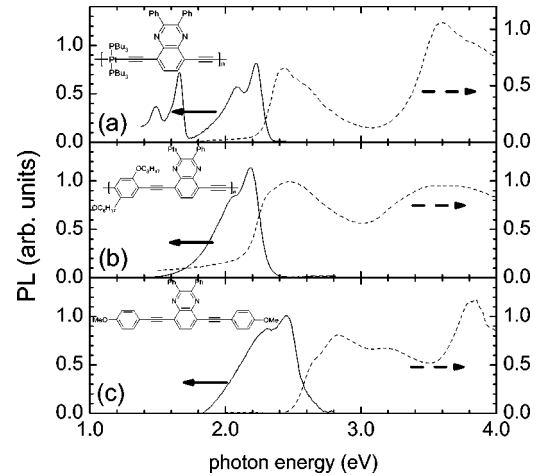


FIG. 1. The photoluminescence (solid lines) spectra at 10 K and absorption (dashed lines) spectra at room temperature of the (a) Pt-containing polymer, (b) organic polymer, and (c) monomer. The insets show the molecular structures of the three materials.

excite the film sample and the other to probe the modulated changes, ΔT in the optical transmission, T . The PA spectrum was obtained by dividing $(-\Delta T/T)$.

The effect of spin-dependent polaron recombination on the PA bands in the PA spectrum was studied by the PADMR technique.¹² In this technique we measure the changes, δT , that are induced in ΔT by resonant μ -wave absorption in magnetic field, H . δT is proportional to δN that is induced in the polaron density N , due to changes in the polaron pair recombination rates. In this work we show H -PADMR spectra, where δT is measured at a fixed probe wavelength as the magnetic field H is scanned. The photoluminescence (PL)-detected magnetic-resonance (PLDMR) technique is closely related to PADMR: PLDMR measures changes, δPL , induced in PL upon magnetic resonance. We note that ODMR experiments are performed at low temperature, because (a) the polaron lifetime is sufficiently long for studies using continuous-wave spectroscopies only at low temperatures and (b) the spin-lattice relaxation time becomes very long at low temperatures, such that the spin alignment is conserved during exciton formation. Resonant absorption of microwave photons, on the other hand, leads to spin randomization. The excitation wavelength was 488 nm (Ar^+ laser) at 200 mW/cm^2 on the sample. A tungsten lamp (10 W) was used as the probe light. The μ -wave power in the cavity is 100 mW. The ODMR experiment is described in detail in recent review papers.^{13,14}

III. EXPERIMENTAL RESULTS

Figure 1 shows the PL spectra at 10 K and absorption spectra at 300 K of the (a) Pt-containing polymer, (b) organic polymer, and (c) monomer. It is seen in Fig. 1(a) that the PL spectrum for the Pt-containing polymer contains a high- and low-energy band that are due to, respectively, singlet and triplet emissions. In addition, the onset of the PL and absorption spectra for the Pt-containing polymer [Fig. 1(a)] occurs at similar values as in the organic polymer [Fig. 1(b)]. This

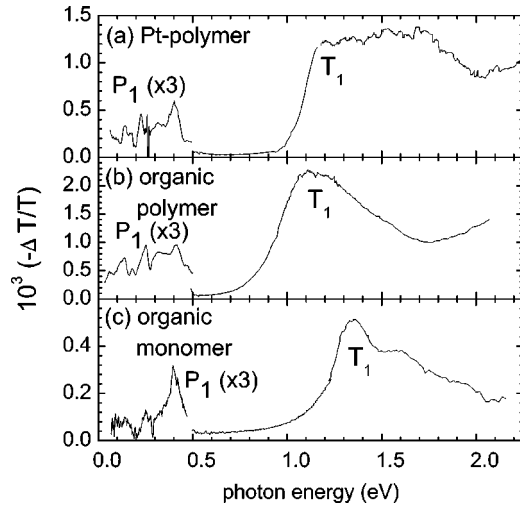


FIG. 2. The PA spectra of the (a) Pt-containing polymer, (b) organic polymer, and (c) monomer at 10 K.

shows that the π conjugation is not interrupted by the Pt atom. Figure 1(b) also shows that the PL and absorption spectra for the organic polymer are redshifted with respect to those for the monomer [Fig. 1(c)]. This is entirely expected, since it is well known that the emission spectra redshift with increasing CL.¹⁵ Figure 1 demonstrates, therefore, that the Pt-containing polymer and organic polymer, respectively, have a similar CL, which is larger than that of the monomer.

Figure 2 shows the PA spectra of the (a) Pt-containing polymer, (b) organic polymer, and (c) monomer at 10 K. These spectra display features similar to the PA spectra of other π -conjugated semiconductors: the low-energy band P_1 is due to photogenerated polarons; whereas the PA band T_1 is due to triplet excitons. We note that T_1 in Pt-containing and organic polymer occur at the same photon energy; although in the Pt-containing polymer it appears to have multiple components. Such high-energy shoulders to T_1 , possibly related to the polaron high-energy band, have previously been observed in other Pt-containing polymers.¹⁶ Moreover, the shift in energy of the triplet band in the PA spectra between the organic monomer and polymer [Figs. 2(b) and 2(c)] is similar in size to that in the corresponding Pt-containing polymer and monomer.¹⁷ This again confirms the longer (and similar) CL in the two polymers.

We now turn to the polaron bands in the PA spectra. The PA spectrum for the monomer film [Fig. 2(c)] shows that P_1 peaks at ≈ 0.4 eV, and quickly goes to zero intensity at smaller photon energies. In contrast, the P_1 bands for the two polymers [Figs. 2(a) and 2(b)] extend down to the lowest photon energies.¹⁸ This is indicative of the much longer CL for the polymers compared to that in the monomers.¹⁹

We have previously shown⁴ that if there is no other spin-randomization process, except the microwave absorption, the value of r can be determined from the intensity of the spin-1/2 PADMR response at the P_1 band under saturation conditions. Specifically,

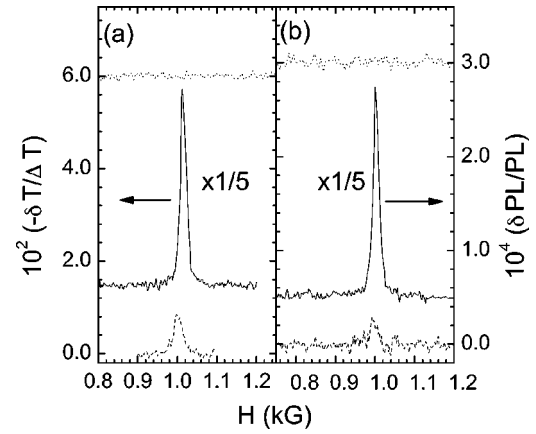


FIG. 3. The 10-K photoinduced absorption detected magnetic-resonance (PADMR) spectra (a) and the photoluminescence detected magnetic-resonance (PLDMR) spectra (b) of Pt-containing polymer (dotted lines), organic polymer (solid lines), and monomer (dashed lines). The base lines are offset for clarity.

$$r = \frac{1 + 3 \left| \frac{\delta T}{\Delta T} \right|^{1/2}}{1 - \left| \frac{\delta T}{\Delta T} \right|^{1/2}}, \quad (2)$$

therefore $r=1$ corresponds to zero PADMR signal, where $\delta T=0$. We measured $|\delta T/\Delta T|$ at P_1 (using appropriate optical filters) in the polymer and monomer films. Figure 3(a) shows the PADMR spectra of Pt-containing polymer, organic polymer, and monomer at 10 K. We obtain $|\delta T/\Delta T|=21\%$ and $r=4.4$ from Eq. (2) for the polymer, and $|\delta T/\Delta T|=0.8\%$ and $r=1.4$ for the monomer. From these values and using Eq. (1), we can calculate the predicted η_{\max} for the polymer and monomer device to be 60% and 32%, respectively. These predictions are very close to the actual values measured by Wilson *et al.*⁵ in the Pt-containing polymer and monomer, namely 57% and 22%, respectively.

The same model rate equations that allow us to calculate the relation between r and $\delta T/\Delta T$ in the PADMR experiment also predict that a positive resonant signal $\delta PL/PL$ should be observed in the PLDMR experiment.⁹ Again $r=1$ corresponds to zero PLDMR signal. It is, however, not straightforward⁹ to obtain a quantitative value of r from PLDMR. Figure 3(b) shows the PLDMR spectra of Pt-containing polymer, organic polymer, and monomer at 10 K. In striking agreement with the measured PADMR resonances, it is seen that the PLDMR response of the polymer exceeds that of the monomer more than 40-fold. This observation confirms our conclusions from PADMR. Conversely, it demonstrates that the PADMR and PLDMR signals are both due to the same mechanism, namely spin-dependent exciton formation, as we also concluded previously.⁹ We emphasize that $\eta_{\max} > 25\%$ in OLEDs requires both $r > 1$, as well as a viable spin-randomization process. Conversely, the observation that $\eta_{\max} > 25\%$ in OLEDs is a testament of the presence of spin-randomization processes during OLED operation. This suggests that ODMR signals should be absent when such experiments are performed in live OLEDs. Indeed

the measured electroluminescence-detected magnetic-resonance signals^{20,21} are roughly three orders of magnitude smaller than the predicted signal strength.⁸

Figure 3 also shows that no PADMR or PLDMR resonances are observed in the Pt-containing polymer (the entire field range up to 4 kG was studied). This was to be expected since the spin-orbit coupling due to Pt leads to spin randomization of polarons.

IV. SUMMARY

We measured the spin-1/2 optically detected magnetic-resonance response of a π -conjugated polymer sample and its corresponding monomer, and compare our conclusions to electroluminescence techniques. *The magnetic-resonance response of the polymer sample was roughly 30 times stronger than that of the monomer.* Based on our previous work, this shows that, whereas exciton formation is spin dependent in the polymer, it is approximately spin independent in the

monomer. We predict a singlet exciton yield of approximately 60% and 30% in the polymer- and monomer-based OLEDs, respectively. These results, obtained by purely optical spectroscopy on films, are very close to the values measured by Wilson *et al.* in working OLEDs made from the Pt-containing derivatives of the materials studied here.⁵ We consider the very good agreement obtained between two different, independent, experimental approaches to confirm and strengthen these techniques and their appropriate conclusions.

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¹⁸The polymer spectra also show a small peak at 0.4 eV similar to the P_1 band in the monomer. This suggests that small amounts of unpolymerized monomer may be present in the polymer samples. However, this can be excluded based on the chemical synthesis route used. We therefore conjecture that the signal at 0.4 eV may be caused by end groups of the polymer chain.

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